

Method for producing an ultraphobic surface by sandblasting

The present invention relates to a method for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, and to the surface obtained thereby and its use described. In the method, the surface of the support material is roughened with a fluid jet containing solid blasting agents, optionally coated with an adhesion promoter layer and then provided with a hydrophobic coating.

Ultraphobic surfaces are characterized by the fact that the contact angle of a drop of liquid, usually water, on the surface is significantly more than 90° and that the roll-off angle does not exceed 10° . Ultraphobic surfaces having a contact angle of $> 150^\circ$ and the abovementioned roll-off angle have a very great technical advantage because, for example, they are not wettable with water or with oil, and soil particles adhere to these surfaces only very poorly and these surfaces are self-cleaning. Here, self-cleaning means the ability of the surface to readily give up soil or dust particles adhering to the surface to liquids which flow over the surface.

There has therefore been no lack of attempts to provide such ultraphobic surfaces. For example, EP 476 510 A1 discloses a method of producing an ultraphobic surface in which a metal oxide film is applied to a glass surface and is then etched using an Ar plasma. However, the surfaces produced using this method have the disadvantage that the contact angle of a drop on the surface is less than 150° .

US 5 693 236 also discloses a plurality of methods for producing ultraphobic surfaces, in which zinc oxide microneedles are applied to a surface using a binder and are then partially uncovered in various ways (e.g. by plasma treatment). The surface structured in this way is then coated with a water-repelling composition. However, surfaces structured in this way likewise only have contact angles of up to about 150° .

The object is therefore to provide ultraphobic surfaces, and a method for their production, which have a contact angle of $\geq 150^\circ$, and a roll-off angle of preferably $\leq 10^\circ$.

5 In this context, the roll-off angle is the angle of inclination of a fundamentally planar but structured surface toward the horizontal at which a stationary drop of water of volume $10 \mu\text{l}$ is moved as a result of the gravitational force when the surface is inclined.

10 The object is achieved according to the invention by the provision of a method, which is the subject-matter of the invention, for producing an ultraphobic surface on metal, glass, ceramic or plastic or a composite of metal and plastic as support material, characterized in that the surface of the support material is intensively roughened with a fluid jet containing solid blasting agents over a relatively long
15 period, the blasting agent having a particle size of $< 200 \mu\text{m}$, optionally coated with an adhesion promoter layer and then provided with a hydrophobic, in particular an oleophobic, coating.

20 For the purposes of the invention, the substrate which may be used is any plastic, any metal, and a composite of metal and plastic. Further substrates (support material) which may be used are ceramic or any materials provided with a ceramic coating, stone-like surfaces, and glass. The substrate can have any desired shape.

25 The fluid jet can be formed by any liquids, in particular water or any gases, in particular air.

The solid blasting agent used as additive to the fluid jet may be any granular substance of high hardness which is known to the person skilled in the art. However, the blasting agent preferably has an average particle size of $< 130 \mu\text{m}$.

30 The particle size of the blasting agent is preferably at least $2 \mu\text{m}$, particularly preferably at least $5 \mu\text{m}$, very particularly preferably at least $20 \mu\text{m}$.

The structures in the surface of the support material produced by sandblasting have depressions in the order of magnitude of from 2 μm to 500 μm , in particular from 5 μm to 200 μm .

- 5 Surprisingly, the effect of the ultraphobic properties of the treated surfaces is codetermined by the partial incorporation of the blasting agent into the surface of the support material.

- 10 The blasting agent is likewise preferably a metal oxide powder, in particular corundum, very particularly preferably a crude, i.e. unused, corundum with sharp-edged particles.

- 15 The substrate is preferably uniformly roughened using a blasting device which produces a fluid jet and in which fluid and blasting agent are mixed by guiding a jet nozzle over the substrate surface in a grid pattern.

- 20 The blasting pressure is preferably 3 to 7 bar and the distance of the jet nozzle from the substrate surface is 1 to 3 cm for a nozzle diameter of e.g. 1 to 2 mm. The treatment time is in this case, in particular, about 0.1 to 10 min for an area of 1 cm^2 .

After the sandblasting, the surfaces thus obtained are provided with a hydrophobic or, in particular, oleophobic coating.

- 25 For the purposes of the invention, a hydrophobic material is a material which, on a level unstructured surface, has a contact angle based on water of more than 90°.

For the purposes of the invention, oleophobic material is a material which, on a level unstructured surface, has a contact angle based on long-chain n-alkanes, such as n-decane, of more than 90°.

- 30 The ultraphobic surface preferably has a coating with a hydrophobic phobicization auxiliary, in particular an anionic, cationic, amphoteric or nonionic, surface-active

compound. Monomeric or polymeric compounds containing a functional group which produces adhesion promotion to the substrate and has a hydrophobic radical are suitable. Suitable hydrophobic radicals are alkyl radicals, fluorinated alkyl radicals or siloxane groups.

5

Compounds to be regarded as phobicization auxiliaries are surface-active compounds of any molar mass. These compounds are preferably cationic, anionic, amphoteric or nonionic surface-active compounds, as listed, for example, in the directory "Surfactants Europa, A Dictionary of Surface Active Agents available in Europe, edited by Gordon L. Hollis, Royal Society of Chemistry, Cambridge, 1995.

10

Examples of anionic phobicization auxiliaries are: alkylsulfates, ether sulfates, ether carboxylates, phosphate esters, sulfosuccinate, sulfosuccinate amides, paraffinsulfonates, olefinsulfonates, sarcosinates, isothionates, taurates and lingnin-based compounds.

15

Examples of cationic phobicization auxiliaries are quaternary alkylammonium compounds and imidazoles

20 Amphoteric phobicization auxiliaries are, for example, betaines, glycines, propionates and imidazoles.

Examples of nonionic phobicization auxiliaries are: alkoxylates, alkyloamides, esters, amine oxides and alkyl polyglycosides. Also suitable are: reaction products of
25 alkylene oxides with alkylatable compounds, such as, for example, fatty alcohols, fatty amines, fatty acids, phenols, alkylphenols, arylalkylphenols, such as styrene/phenol condensates, carboxamides and resin acids.

In the case of the monomolecular phobicization auxiliaries, preference is given to
30 those in which 1 to 100%, particularly preferably 60 to 95%, of the hydrogen atoms have been substituted by fluorine atoms. Examples which may be mentioned are perfluorinated alkylsulfate, perfluorinated alkylsulfonates, perfluorinated

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alkylphosphonates, perfluorinated alkylphosphinates and perfluorinated carboxylic acids.

As polymeric phobicization auxiliaries for the hydrophobic coating or as polymeric hydrophobic material for the surface, preference is given to using compounds with a molar mass M_w of > 500 to 1,000,000, preferably 1000 to 500,000 and particularly preferably 1500 to 20,000. These polymeric phobicization auxiliaries can be nonionic, anionic, cationic or amphoteric compounds. The polymeric phobicization auxiliaries can contain groups which effect adhesion promotion to the substrate and/or contain groups which are self-crosslinking or can be crosslinked using an external curing agent. In addition, these polymeric phobicization auxiliaries may be homo- and copolymers, graft polymers and graft copolymers, and random copolymers.

The polymeric phobicization auxiliaries preferably contain alkyl groups,

perfluorinated alkyl groups or siloxane groups, (e.g. $\begin{array}{c} \text{R} \quad \text{R} \\ | \quad | \\ \text{---Si---O---Si---} \\ | \quad | \\ \text{R} \quad \text{R} \end{array}$ units where R = $\text{C}_1\text{-C}_4\text{-alkyl}$, preferably methyl).

Particularly preferred polymeric phobicization auxiliaries are those of the type AB, BAB and ABC block polymers. In the AB or BAB block polymers, the A segment is a hydrophilic homopolymer or copolymer, and the B block is a hydrophobic homopolymer or copolymer or a salt thereof.

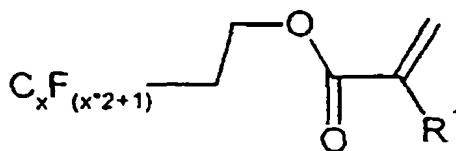
Particular preference is also given to anionic, polymeric phobicization auxiliaries, in particular condensation products of aromatic sulfonic acids with formaldehyde and alkylnaphthalenesulfonic acids or of formaldehyde, naphthalènesulfonic acids and/or benzene sulfonic acids, condensation products of optionally substituted phenol with formaldehyde and sodium bisulfite.

Also preferred are condensation products obtainable by reacting naphthols with alkanols, adding alkylene oxide and at least partially converting the terminal

hydroxyl groups into sulfo groups or monoesters of maleic acid and phthalic acid or succinic acid.

In another preferred embodiment, the phobicization auxiliary is [lacuna] from the group of sulfosuccinates and alkylbenzenesulfonates. Also preferred are sulfated, alkoxyated fatty acids or salts thereof. Alkoxyated fatty acid alcohols means, in particular, those C₆-C₂₂-fatty acid alcohols which are saturated or unsaturated and have 5 to 120, 6 to 60, very particularly preferably 7 to 30, ethylene oxide units, in particular stearyl alcohols. The sulfated alkoxyated fatty acid alcohols are preferably in the form of a salt, in particular an alkali metal or amine salt, preferably diethylamine salt.

Hydrophobic monomers used for the preparation of the polymeric phobicization auxiliaries are compounds of the formula



where x is a natural number from 6 to 12 and

R¹ is hydrogen or methyl, stearyl methacrylate or behenyl methacrylate.

Monomers used for introducing the group promoting adhesion to the substrate are, for example, vinylphosphonic acid, mono(hydroxyethyl methacrylate) phosphate, vinylphenylphosphonic acid, trimethoxyvinylsilane, trimethoxysilylpropyl methacrylate, vinylsilatrane, diethylaminoethyl methacrylate, acrylic acid, methacrylic acid, itaconic anhydride or maleic anhydride.

Monomers used for introducing a self-crosslinking group are, for example, trimethoxysilylpropyl methacrylate or trimethoxyvinylsilane (silane-functional).

Special functional monomers are used to permit crosslinking of the polymer layer.

The acetoacetate group is crosslinkable with di- or polyamines, di- or polyisocyanates or di- or polyacrylates (Michael addition). They are introduced via the monomer methacryloyloxyethyl acetoacetate.

- 5 The epoxy group is crosslinkable with amines or anhydrides. Its introduction is possible via the monomer glycidyl methacrylate.

- The isocyanate group is crosslinkable with di- or polyacetoacetates, di- or polyols, di- or polyamines or compounds containing at least two azomethine groups. Their
10 introduction is possible via α,α -dimethyl-3-isopropenyl-benzyl isocyanate or isocyanatoethyl methacrylate.

- The hydroxyl group is crosslinkable with di- or polyisocyanates, melamine resins or urea resins. It can be introduced via hydroxypropyl methacrylate, hydroxypropyl
15 methacrylate, hydroxybutyl methacrylate, hydroxyethyl methacrylate or hydroxyethyl acrylate.

- The anhydride group is crosslinkable with di- or polyols or di- or polyamines. Its introduction is possible using itaconic anhydride or maleic anhydride.

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For the crosslinking, it is also possible to use two polymeric phobicization auxiliaries in a mixture or in a two-coat application which have groups which react with one another.

- 25 In addition, the isocyanate-, epoxy- or anhydride-functional polymers can be reacted with hydroxyethyl acrylate or methacrylate. The resulting (meth)acrylate-functional resins are free-radically (photochemically, by electron beams or free-radical initiators) crosslinkable.

- 30 During the preparation, 0 - 50% by weight of monomers which are neither adhesion-promoting, hydrophobic or crosslinking can be added to the polymeric phobicization

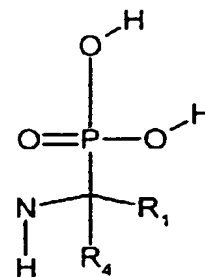
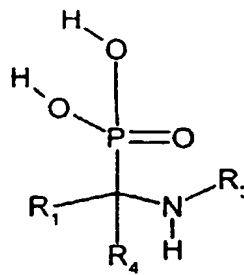
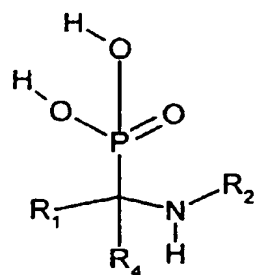
auxiliaries. Examples thereof are styrene, methyl methacrylate, butyl acrylate, butyl methacrylate, ethylhexyl methacrylate, methyl acrylate or ethyl acrylate.

5 The polymeric phobicization auxiliaries are preferably prepared by free-radical polymerization in the presence of an initiator (peroxy or azo compound) in a solvent. For polymeric phobicization auxiliaries which contain perfluoroalkyl groups, preference is given to ketones, such as, for example, butanone, methyl isobutyl ketone or cyclohexanone.

10 To improve the adhesion of the hydrophobic or oleophobic coating to the sandblasted substrate, it may be advantageous to firstly coat the surface of the sandblasted substrate with an adhesion promoter layer. Therefore, an adhesion promoter layer is optionally applied between the surface and the hydrophobic or oleophobic coating. In principle, the adhesion promoter may be any substance known to the person skilled in
15 the art which increases the bonding between the surface and the respective hydrophobic or oleophobic coating. Preferred adhesion promoters, e.g. for thiols as a hydrophobic coating, are layers of noble metals, e.g. of Au, Pt or Ag or those of GaAs, in particular of gold. The thickness of the adhesion promoter layer is preferably 10 to 100 nm.

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Preferred adhesion promoters for functional polymeric phobicization auxiliaries are vinylphosphonic acid, mono(hydroxyethyl methacrylate) phosphate, allylphosphonic acid, allylamine, maleic anhydride, acrylic acid, allyl sulfide, trimethoxyvinylsilane, trimethoxysilylpropyl methacrylate, trimethoxysilylpropyl mercaptan,
25 glycidyloxypropoxypropyltrimethoxysilane, diethylaminoethyl methacrylate and aminophosphonic acids. Preference is given to aminophosphonic acids of the formulae



where

R₁ and R₄ are hydrogen, C₁-C₂₂-alkyl or C₆-C₁₀-aryl, preferably hydrogen or phenyl,

5

R₃ is C₂-C₂₂-alkylene or C₅-C₂₀-cycloalkylene and

R₂ is hydrogen or C₁-C₂₂-alkyl.

10 Using the method according to the invention it is possible to prepare ultraphobic surfaces for which the contact angle of a drop on the surface is $\geq 155^\circ$. The invention therefore also provides the ultraphobic surfaces obtained by the method according to the invention.

15 These ultraphobic surfaces have the advantage, inter alia, that they are self-cleaning, self-cleaning taking place when the surface is exposed from time to time to rain or moving water. As a result of the ultraphobic surface, the drops of water roll off the surface, and soil particles, which adhere only very poorly to the surface, settle on the surface of the drops which are rolling off and are thus removed from the ultraphobic surface. This self-cleaning is effective not only upon contact with water but also with oil.

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There are a large number of industrial use possibilities for the surface produced by the method according to the invention. Also claimed, therefore, are the following uses of the ultraphobic surfaces produced by the method according to the invention:

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Hulls of ships can be coated with the ultraphobic surface produced by the method according to the invention in order to reduce their resistant to friction.

As a result of the fact that water does not adhere to the ultraphobic surface produced
5 by the method according to the invention, it is suitable as a rust inhibitor for base metals of any type.

In addition, sanitary installations, in particular toilet bowls, can be provided with the ultraphobic surface produced by the method according to the invention in order to
10 reduce their susceptibility to soiling.

A further use of the ultraphobic surface is the coating of surfaces to which water must not adhere in order to avoid icing over. Examples which may be mentioned here are the surfaces of heat exchangers, e.g. in refrigerators, or the surfaces of aircraft.
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The surfaces produced by the method according to the invention are also suitable for fixing to house façades, roofs, monuments in order to render these self-cleaning.

The ultraphobic surfaces produced by the method according to the invention are also
20 suitable, in particular, for the coating of moldings which are transparent. In particular, these may be transparent glazings of buildings, vehicles, solar collectors. For this, a thin layer of the ultraphobic surface according to the invention is applied to the molding by vapor deposition.

25 The invention also provides a material or construction material having an ultraphobic surface according to the invention.

The invention further provides for the use of the ultraphobic surface according to the invention for the friction-reducing lining of vehicle bodies, aircraft fuselages or hulls.
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The invention also provides for the use of the ultraphobic surface according to the invention as self-cleaning coating or paneling of building structures, roofs, windows, ceramic construction material, e.g. for sanitary installations, household appliances.

- 5 The invention further provides for the use of the ultraphobic surface according to the invention as an antirust coating of metal objects.

The method according to the invention is illustrated below by reference to examples.

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Examples

Example 1

- 5 An extruded polymethyl methacrylate sheet with an area of $10 \times 10 \text{ mm}^2$ and a thickness of 3 mm was sandblasted using a 3-chamber blasting device (model name: Kermo 3) from Renfert GmbH, D-78245 Hilzingen. The blasting agent used was corundum from Renfert. The fluid used for the fluid jet was air. The blasting agent was unused and had an Al_2O_3 content of $< 99.5\%$ by weight and an average particle
- 10 size of $125 \text{ }\mu\text{m}$. The jet nozzle used was a round nozzle with a diameter of 1.2 mm from Renfert. The polymer sheet was sandblasted with a blasting pressure of 5 bar, the distance of the round nozzle from the polymer surface being 1.5 cm and the jet nozzle being guided over the sheet in a grid pattern. The sheet was treated for 1 minute. The substrate then had irregularly distributed indentations and raised areas
- 15 50 to $200 \text{ }\mu\text{m}$ in size.

The substrate treated in this way was coated with an approximately 50 nm-thick gold layer by atomization. This coating method corresponds to the method which is also customary for the preparation in electron microscopy and is described by Klaus

20 Wetzig, Dietrich Schulze, "In situ Scanning Electron Microscopy in Material Research", page 36-40, Akademie Verlag, Berlin 1995. This literature reference is hereby incorporated as reference and is accordingly to be regarded as part of the disclosure.

- 25 Finally, the gold layer of the sample was coated with a few drops of a solution of n-perfluorooctanethiol in α, α, α -trifluorotoluene (1 g/l) at room temperature in a sealed vessel, then rinsed with α, α, α -trifluorotoluene and dried.

The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume

30 $10 \text{ }\mu\text{l}$ rolls off if the surface is inclined by $< 3^\circ$.

Example 2

5 A titanium sheet $30 \times 30 \text{ mm}^2$ in size and 2 mm in thickness was roughened as in Example 1 using a fluid jet containing corundum, although here a blasting material with an average particle size of $90 \mu\text{m}$ was used. These roughened sheets are cleaned in ethanol and dried in air. They are then immersed in a 0.1% strength solution of phosphate-functional, perfluorinated binding agent (solvent MIBK) for 24 h and then briefly swirled in pure MIBK and then dried at 120°C for 20 h.

10 The binder is prepared as follows:

I. Phosphonate-functional perfluorinated binder

15 70 g of perfluorinated acrylate (Zonyl TA-N®), 25 g of methacryloyloxyethyl acetoacetate, 5 g of a 50% strength aqueous solution of vinylphosphonic acid, 100 g of methyl iso-butyl ketone, 1 g of azobisisobutyronitrile and 5 g of an ethoxylated nonylphenol (with 20 ethylene oxide units) are mixed, and the solution is allowed to run into a flask heated to 90°C in 2 hours. 3 ml of triethylamine are added and the mixture is then stirred for 6 hours.

20

The surface has a static contact angle for water of $> 150^\circ$. A drop of water of volume $10 \mu\text{l}$ rolls off if the surface is inclined by $< 10^\circ$.

Example 3

25

A titanium sheet $30 \times 30 \text{ mm}^2$ in size and 2 mm in thickness was roughened as in Example 1 using a fluid jet containing corundum, although here a blasting material with an average particle size of $90 \mu\text{m}$ was used. These roughened sheets are cleaned in ethanol and dried in air. They are then immersed in a 0.1% strength solution of silane-functional perfluorinated binder (solvent MIBK) for 24 h and then briefly swirled in pure MIBK and then dried at 120°C for 20 h.

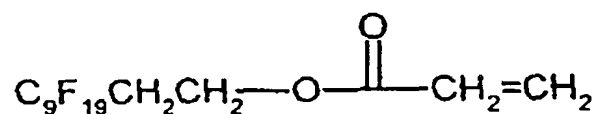
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The binder is prepared as follows:

The mixture of 70 g of perfluorinated acrylate, 30 g of trimethoxysilylpropyl methacrylate, 1 g of azobisisobutyronitrile and 100 g of methyl butyl ketone is heated at 65°C for 16 h. Prior to application, 0.1% by weight, based on the polymer mass, of dodecylbenzenesulfonic acid is also added to this solution.

II. Silane-functional perfluorinated binder

- 10 The perfluorinated acrylate is an acrylate containing a fluorinated C₆-C₁₂-radical and corresponding to an average structural formula:



The surface has a static contact angle for water of > 150°. A drop of water of volume 10 µl rolls off if the surface is inclined by < 10°.

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Example 4

- A titanium sheet 30 × 30 mm² in size and 2 mm in thickness was roughened as in Example 1 using a fluid jet containing corundum, although here a blasting material with an average particle size of 90 µm was used. These roughened sheets are cleaned in ethanol and dried in air. They are then immersed in a 0.1% strength solution of aminophosphonic acid in butanol for 24 h and then briefly swirled in pure MIBK and then dried at 120°C for 1 h. To the adhesion promoter layer applied in this way is applied a 0.1% strength solution of epoxy-functional perfluorinated binder (solvent MIBK) by homogenous spraying with an atomizer attachment for measuring cylinders with ground-glass joints (Görres; initial pressure 2 bar of N₂) from a distance of about 20 cm. The sheet is then dried at 120°C for 20 h.

The aminophosphonic acid is prepared as follows:

III. Aminophosphonic acid dissolved in butanol

The mixture of 11.6 g of 1,6-diaminohexane, 212 g of benzaldehyde, 500 g of butanol and 1 g of phosphorous acid is boiled for 8 hours at the water separator for light solvents. 164 g of phosphorous acid are added, and the mixture is heated for 2 hours at 120°C.

The binder is prepared as follows:

IV. Epoxy-functional perfluorinated binder

The mixture of 60 g of perfluorinated acrylate, 20 g of styrene, 20 g of glycidyl methacrylate. 1 g of azobisisobutyronitrile and 100 g of butanone is heated at 65°C for 16 hours.

The surface has a static contact angle for water of $> 150^\circ$. A drop of water volume 10 μl rolls off if the surface is inclined by $< 10^\circ$.

Example 5

In this example a 2 mm-thick titanium sheet was roughened exactly as in Example 1 using a fluid jet containing corundum.

The sheet treated in this way was immersed in a 1% strength by weight solution of Fluowet PL80 (mixture of perfluorinated phosphanates and phosphinates) from Clariant for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 3^\circ$.

Example 6

In this example a 2 mm-thick V4A stainless steel sheet was roughened exactly as in Example 1 using a fluid jet containing corundum.

5

The sheet treated in this way was immersed into a 1% strength by weight solution of Fluowet PL80 from Clariant for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

- 10 The surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 5^\circ$.

Example 7

- 15 In this example a 2 mm-thick titanium sheet was roughened as exactly as in Example 1 with a fluid jet containing corundum.

The sheet treated in this way was immersed in a 1% strength by weight solution of Hoe S2746 (mixture of perfluorinated phosphonates and phosphinates) from Clariant

- 20 for 5 hours at pH 7 and then rinsed with water and dried at 60°C.

The surface has a static contact angle for water of $> 160^\circ$. A water droplet of volume 10 μl rolls off if the surface is inclined by $< 5^\circ$.

25 **Example 8**

In this example a 2 mm-thick titanium sheet was treated exactly as in Example 1. In this example too the surface has a static contact angle for water of $> 160^\circ$. A drop of water of volume 10 μl rolls off if the surface is inclined by $< 3^\circ$.

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